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L4   ANSWER 1 OF 4  CAPLUS  COPYRIGHT 2002 ACS
AN   2000:289281  CAPLUS
DN   132:279473
TI   Process for conversion of oxidized sugars into hydrogenated sugars via
     catalytic hydrogenation
IN   Fleche, Guy; Fuertes, Patrick; Tamion, Rodolphe
PA   Roquette Freres, Fr.
SO   Fr. Demande, 19 pp.
     CODEN: FRXXBL
DT   Patent
LA   French
FAN.CNT 1
     PATENT NO.       KIND  DATE           APPLICATION NO.  DATE
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PI   FR 2784382        A1   20000414       FR 1998-12791    19981013
     EP 999197         A2   20000510       EP 1999-402486   19991011
         R:  AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
             IE, SI, LT, LV, FI, RO
PRAI FR 1998-12791          19981013

L4   ANSWER 2 OF 4  CAPLUS  COPYRIGHT 2002 ACS
AN   1958:37819  CAPLUS
DN   52:37819
OREF 52:6790f-h
TI   Spent sulfite liquor studies. V. Isolation of crystalline sugars from
     softwood spent sulfite liquor solids via isopropylidene derivatives
AU   Boggs, Lawrence A.
CS   Sulfite Pulp Mfrs. Research League, Appleton, WI
SO   Tappi (1957), 40, 752-5
DT   Journal
LA   Unavailable

L4   ANSWER 3 OF 4  CAPLUS  COPYRIGHT 2002 ACS
AN   1957:98810  CAPLUS
DN   51:98810
OREF 51:17768g-i,17769a-g
TI   Configuration of glycosidic linkages in oligosaccharides. IV. Further
     degradations of reducing disaccharides to 2-O-glycosylglycerols
AU   Charlson, A. J.; Gorin, P. A. J.; Perlin, A. S.
CS   Natl. Research Council, Saskatoon
SO   Can. J. Chem. (1957), 35, 365-73
DT   Journal
LA   Unavailable

L4   ANSWER 4 OF 4  CAPLUS  COPYRIGHT 2002 ACS
AN   1938:35651  CAPLUS
DN   32:35651
OREF 32:4948h-i,4949a-i
TI   l-Threonic acid-3-methyl ether and l-threonic acid-2,3-dimethyl ether
AU   Gatzi, K.; Reichstein, T.
SO   Helv. Chim. Acta (1938), 21, 195-205
DT   Journal
LA   Unavailable

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QD1, H41

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AB Catalytic **hydrogenation** of oxidized sugars into hydrogenated sugars in presence of Lewis acid, is reported. Thus, ruthenium-catalyzed **hydrogenation** of arabonic acid in presence of 2-anthraquinone sulfonic acid gave arabitol in good yield. L'erythrose, au threose, au sorbose, au xylose, a **l'arabinose**, au ribose, au ribulose, au xylulose, au glucose, au galactose, au fructose, au mannose, au maltose ou au lactose. Erythritol, le threitol, le ribitol, le xylitol, **l'arabitol**, mannitol, le sorbitol, l'iditol, le maltitol, le lactitol.

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AB cf. Wisniewski, et al., C.A. 50, 6044f. Sprucewood spent sulfite liquor dried solids were refluxed with Me2CO contg. a catalytic amt. of concd. H2SO4, to convert the sugars to their di-O-isopropylidene derivs. The main portion of the nonsugars remained insol. and was filtered off. Di-O-isopropylidene D-mannose is sparingly sol. in H2O, from which it was crystd. The di-O-propylidene pentoses were sepd. from the hexose derivs. by 2 methods: mol. distn., and exhaustive steam distn. The acid-sensitive derivs. were sepd. from the acid-resistant derivs. by a partial hydrolysis followed by extn. with CHCl3 of the unaltered resistant derivs. Products thus obtained in pure cryst. form include: di-O-isopropylidene D-mannose, D-xylose, **L-arabinose**, and D-galactose. Catalytic **hydrogenation** of these products yielded sirupy di-O-isopropylidene D-mannitol, which was converted by acid hydrolysis to cryst. D-mannitol, and cryst. xylitol, **L-arabitol**, and dulcitol.

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AB cf. C.A. 51, 14563d. The configuration of the glycoside linkages in various reducing disaccharides was detd. by converting each of these into the corresponding 2-O-glycosylglycerol, the structure of which was then established. All oxidations were carried out in AcOH with Pb(OAc)4; **hydrogenations** with NaBH4. Unless otherwise stated [.alpha.]D27 of substituted hexitols and pentitols were taken in H2O; those of the benzoates were taken in 2,4-lutidine. Benzoates were recrystd. from EtOH at 30.degree.. Sugars produced hydrolytically were characterized by paper chromatograms. Infrared absorption spectra were taken by the KBr window technique, and were often used for purposes of identification; no actual absorption data are included. 3-O-.beta.-L-arabopyranosyl-**L-arabinose** (718 mg.) from larch arabogalactan was oxidized, treated with 10% (CO2H)2, filtered, and the evapd. filtrate dissolved in H2O and decompd. with a mixt. of Amberlite IR-120 and Dowex-1 resins. The product was reduced, treated with AcOH, deionized, evapd., extd. with MeOH, and evapd. to remove H3BO3 giving 415 mg. 2-O-.beta.-L-arabopyranosyl-L-erythritol (I), [.alpha.] 135.degree. (c 1.7); hexabenzoate, m. 131-4.degree., [.alpha.] 114.degree. (c 1.0). I (304 mg.) was oxidized and then reduced as above and the products fractionated on a cellulose column using half-satd. BuOH giving 69 mg. 2-O-.beta.-L-arabopyranosylglycerol, m. 154-5.degree., [.alpha.] 204.degree. (c 1.2); pentabenzoate, m. 48-50.degree., [.alpha.] 164.degree. (c 0.8). Treated similarly, with but slight modifications, 3-O-.alpha.-D-xylopyranosyl-**L-arabinose** (452 mg.), obtained from the autohydrolyzate of golden apple gum, gave 338 mg. 2-O-.alpha.-D-xylopyranosyl-L-erythritol, sirup, [.alpha.] 91.degree. (c 1.5); hexabenzoate, m. 64-7.degree., [.alpha.] 98.degree. (c 1.1). 2-O-.alpha.-D-Xylopyranosylglycerol, sirup, [.alpha.] 91.degree. (c 1.5), after fractionation; pentabenzoate, m. 51-5.degree., [.alpha.] 51.degree. (c 1.1). The partial hydrolysis of wheat flour pentosan gave 4-O-.beta.-D-xylopyranosyl-D-xylose, from which, by the usual procedures were formed 2-O-.beta.-D-xylopyranosylglycerol, [.alpha.] -37.degree. (c 1.1), and the pentabenzoate, m. 51-3.degree., [.alpha.] -36.degree. (c 0.9). Partial hydrolysis of corncob hemicellulose B gave 2-O-.beta.-D-xylopyranosyl-**L-arabinose** (II) from which was obtained, by direct reduction with NaBH4, 2-O-.beta.-D-xylopyranosyl-

L-arabitol, m. 185-7.degree. (from MeOH-EtOH), [.alpha.] -33.degree. (c 1.2), which by oxidation followed by reduction gave 2-O-.beta.-D-xylopyranosylglycerol, [.alpha.] -30.degree. (c 1.3); pentabenzoate, m. 51-3.degree., [.alpha.] -35.degree. (c 1.2). The partial hydrolysis of gum acacia gave 3-O-.alpha.-D-galactopyranosyl-**L-arabinose**, giving rise to 2-O-.alpha.-D-galactopyranosyl-L-erythritol, m. 156-8.degree., [.alpha.] 145.degree. (c 1.0), from which was formed 2-O-.alpha.-D-galactopyranosylglycerol, m. 131-2.degree. (from EtOH), [.alpha.] 164.degree. (c 0.7); hexabenzoate, m. 156-7.degree. [.alpha.] 120.degree. (c 1.4). 3-O-.beta.-D-galactopyranosyl-D-galactose from gum acacia gave 4-O-.beta.-D-galactopyranosyl-D-arabitol, m. 177-9.degree. (from EtOH), [.alpha.] -78.degree. (c 0.6), and from this, 2-O-.beta.-D-galactopyranosylglycerol, sirup, whose amorphous hexabenzoate m. 56-9.degree.(also given as 61-3.degree.), [.alpha.] 36.degree. (c 0.7) (also given as 25.degree. (c 0.6)). From sucrose, by enzymic synthesis with Leuconostoc mesenteroides was formed 5-O-.alpha.-D-glucopyranosyl-D-fructose, which by oxidation and subsequent reduction gave 2-O-.alpha.-D-glucopyranosylglycerol, [.alpha.] 119.degree. (c 0.7); hexabenzoate, m. 137-8.degree. [.alpha.] 94.degree. (c 0.8, CHCl3). A mixt. of 8.4 g. tri-O-acetyl-.beta.-L-arabopyranosyl bromide, 7.5 g. 1,3-O-benzylideneglycerol (III), 20 g. Ag2O, 50 g. Drierite, and 125 ml. C6H6 was shaken 3 hrs. at 55.degree., then refluxed 0.25 hr., filtered, and treated with 200 ml. CHCl3 and 0.5 g. MeONa in 20 cc. MeOH. After 18 hrs. at 20.degree., the mixt. was evapd. to a sirup and fractionated on cellulose. Unchanged III was eluted by C6H6 and C6H6-EtOH (3:1, contg. a trace H2O) was used in eluting 1',3'-benzylidene-2-O-.alpha.-L-arabopyranosylglycerol (IV), m. 121-2.degree. (from MeOH-Et2O), [.alpha.] 4.degree. (c 1.1, EtOH). IV (46 mg.) in 0.3 ml. CHCl3 and 0.2 ml. pyridine was treated with 0.12 ml. BzCl; after 18 hrs. CHCl3 and MeOH were added and the mixt. washed with 1% H2SO4, aq. NaHCO3, and H2O, dried, filtered, and evapd. giving the tribenzoate of IV, m. 170-2.degree. (softening 160-65.degree.), [.alpha.] 114.degree. (c 0.9). IV (28 mg.) shaken 18 hrs. with PdO and H gave 2-O-.alpha.-L-arabopyranosylglycerol, a sirup, [.alpha.] 5.degree. (c 10, H2O), whose pentabenzoate m. 53-7.degree., [.alpha.] 93.degree. (c 0.9). The present results confirm the configurations previously assigned to the various disaccharides, with the exception of II, which was believed to have the .alpha.-configuration; the present data characterize the compds. more fully than do those previously obtained from equil. rotation values. Because of the relatively good agreement in the results reached by the 2 methods, however, the validity of the polarimetric technique is supported.

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AB The degradation of acetone-l-ascorbic acid (C. A. 29, 5076.3) and the partial methylation of l-threonic acid lactone (C. A. 32, 915.4) give 2-methyl-l-threonic acid. For purposes of comparison the isomeric 3-Me ether (I) has been prepd. Attempts were made to produce I from the acetone-l-threose (II) of known structure by methylation, cleavage and Br oxidation. The product decompd. entirely on distn. in a high vacuum below 100.degree., probably on account of a small amt. of impurity acting catalytically. Catalytic **hydrogenation** of 5 g. **l-arabinose** in 40 cc. H2O in the presence of Raney Ni (from 3 g. Ni-Al alloy) for 40 hrs. with the use of 745 cc. H2 gave 4.5 g. of **l-arabitol**, m. 99-101.degree. (cor.). Degradation of benzal-**l-arabitol** with Pb (OAc)4 yielded cryst. benzal-l-threose, C11H12O4.0.5 H2O, m. 119-20.degree. (cor.) from benzene-Et2O. A mixt. of 4.0 g. II, 25 g. Ag2O (dried in a high vacuum over P2O5) and 23 g. MeI was slowly rotated in a glass-stoppered flask with 35 cc. anhyd. Et2O. The reaction mixt. was refluxed at 50.degree. for 8 hrs., treated with 13 g. Ag2O, 11 g. MeI and 10 cc. abs. Et2O and again refluxed for 6 hrs. A further similar addn. was made and the refluxing was carried out at 55.degree.. The methylated product was extd. with 400 cc. abs. Et2O, the ext. was filtered and evapd. down, and the residue (4.5 g.) was distd. in vacuo, yielding 4.2 g. of sirupy

1,2-acetone-l-threose 3-Me ether, C8H14O4, b12 87-9.degree., cleaved by heating on the steam bath for 1.5 hrs. with 80 cc. of 10% AcOH to 3.1 g. of faintly bright yellow sirup, l-threose 3-Me ether (III). Oxidation of III in 50 cc. H2O by shaking with 3.8 g. Br, neutralization with Ag2CO3 and further working up gave 2.6 g. of non-reducing colorless sirup which decompd. at 80-90.degree. (bath temp.) on high-vacuum distn. Although I might be prepd. in this way under special conditions, ethylidene-l-threonic acid (IV) provided a more accessible starting material. The Me ester of IV (3 g.) was methylated with dry Ag2O and MeI in Et2O to give Me ethylidene-l-threonate 3-Me ether (V), C8H14O5, m. 49-50.degree. (cor.), [.alpha.]D19 46.4 .+-. 2.degree. (in MeOH). Cleavage of 0.48 g. V with 7 cc. of 5% NaOH in aq. MeOH for 30 min. on the steam bath gave 260 mg. of the corresponding acid (VI), C7H12O5, m. 158-61.degree. (cor.), [.alpha.]D20 70.7 .+-. 2.degree. (in H2O), subliming in a high vacuum at 95.degree. to yield granules, m. 161.5-2.0.degree. (changing to long needles at 120.degree.), quantitatively converted by methylation with CH2N2 to V. Cleavage of 0.70 g. V with 20 cc. of 10% AcOH by heating on the steam bath for 4 hrs. produced 0.45 g. of l-threonic lactone 3-Me ether (VII), b0.12 83.degree., [.alpha.]D21 19.8 .+-. 2.degree. (in MeOH), which was similarly prepd. from VI. For the sake of comparison 50 mg. of the Me ester of IV was treated with 5 cc. of MeOH satd. with NH3 at 0.degree. and stood at room temp. for 3 days. After evapg. to dryness, the residue was crystd. from AcOEt, yielding large fibrous leaflets of ethylidene-l-threonic amide, m. 155-6.degree., [.alpha.]D19 103.0 .+-. 2.degree. (in MeOH). Analogous treatment of 40 mg. V produced small granules of ethylidene-l-threonic amide 3-Me ether, m. 114-16.degree., [.alpha.]D19 22.8 .+-. 2.degree. (in MeOH), and similarly VII was converted into the extremely hygroscopic l-threonic amide 3-Me ether, C5H11NO4, m. about 78-81.degree., [.alpha.]D18 57.4 .+-. 3.degree. (in MeOH), which is quite distinct from the known amide of l-threonic acid 2-Me ether. Methylation of 0.45 g. VII in 3 cc. anhyd. dioxane with a large excess of CH2N2 in Et2O according to the method of Schmidt and Zeiser (C. A. 29, 2150.2) produced 0.26 g. of a viscous colorless sirup of l-threonic lactone 2,3-di-Me ether (VIII), b12 120.degree.; amide, C6H13NO4, m. 148-50.degree., [.alpha.]D20 64.8 .+-. 2.degree. (in MeOH). Methylation of 1.85 g. of l-threonic lactone 2-Me ether with 12 g. dry Ag2O and 10 g. of pure MeI in 10 cc. anhyd. Et2O by heating for 6 hrs. at 50.degree. and a further treatment with 10 g. Ag2O and 10 g. MeI for 6 hrs. at 55.degree., extn. with 200 cc. Et2O, filtration, evapn. and distn. of the sirup gave 2.1 g. of a mixt. of l-threonic acid 2,3-di-Me ether (IX) and Me threonate 2,3,4-tri-Me ether (X), sepd. by sapon. of 1.0 g. with 5% NaOH which converted IX into VIII (90 mg.) and yielded 0.23 g. of thick, sirupy l-threonic acid 2,3,4-tri-Me ether (XI), b11 147-9.degree., [.alpha.]D20 40.2 .+-. 2.degree. (in MeOH). Treatment of 90 mg. VIII with 10 cc. of NH3 in MeOH, evapn. and crystn. from AcOEt gave the known amide, identical with that prepd. from VIII through VII. Methylation of 0.20 g. XI with CH2N2 in Et2O, evapn. and distn. gave 0.2 g. of the ester X as a thick, water-white oil, b11 102-3.degree., which was converted by NH3 in MeOH to l-threonic amide 2,3,4-tri-Me ether, C7H15NO4, m. 79.degree., [.alpha.]D20 63.7 .+-. 2.degree. (in MeOH). The constitution of IV as 1,3-ethylidene-l-threonic acid is proved by these reactions.